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Dear Client of CCRMP,

The attached report, "Uses of CCRMP Compositional Reference Materials" is being distributed with each order of reference materials. Please contact me with any comments or questions on this report.

Sincerely,

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USES OF CCRMP COMPOSITIONAL REFERENCE MATERIALS

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Uses of CCRMP Compositional Reference Materials

by

Henry F. Steger and Maureen E. Leaver

Abstract

This presentation introduces many of the considerations that a user should take into account in selecting appropriate compositional reference materials for use in assessing an analytical method for accuracy and precision. The impact of these considerations is discussed. The statistical tests provided in ISO Guide 33 "Uses of certified reference *materials*" to assess a method for accuracy and precision are described. Finally these statistical tests are applied to two CCRMP gold reference ores, MA-1b and CH-3, to illustrate the technique.

Uses of CCRMP Compositional Reference Materials

Introduction

Compositional reference materials such as the certified reference ores, concentrates, etc., offered by the Canadian Certified Reference Materials Project are in common use in the analytical laboratories associated with the mineral industry. For our industry, the simplest and possibly best definition of a compositional reference material is that it is a "real" world substance that has been chemically characterized for one or more elements, constituents, etc. with a known uncertainty. "Real" world materials are more complex, chemically, compositionally and structurally, than primary reference standards, which are often pure chemicals. Furthermore their chemical characterization usually has a greater level of uncertainty and is less straightforward in terms of traceability.

This presentation touches on some of the factors of CCRMP reference materials that a user should take into careful consideration in their use.

Properties of Compositional Reference Materials

It is in general true that an analytical laboratory equates the "use" of reference materials with "the agreement between its measured value and the certified value". In fact however, the use of a compositional reference material actually begins in the selection of an appropriate reference material for the purpose.

A compositional reference material has several properties that can influence a user to choose it for a specific purpose. The relative importance of these properties can vary depending on the intended use, i.e., to assess performance or to calibrate an instrument. This presentation is however restricted to the use of compositional reference materials to assess a method for accuracy and precision.

Some of the important properties of compositional reference materials are obvious. For example:

1. the certified elements/constituents;
2. the matrix, i.e., chemical and/or mineralogical composition, and
3. the concentration of the certified elements.

(1) This point seems redundant. Surely a user would not use a reference material certified for, e.g., zinc, to assess performance for lead! However it does occur that a

user cannot find a suitable reference material and in desperation, or possibly ignorance, uses an element with an uncertified value in an available reference material to assess performance. CCRMP received a complaint last year from a client who stated that his use of the value for Al in reference material MP-1a clearly demonstrated that it was too high by ~ 20%. This occurred despite the fact that CCRMP had stated the value for Al was for general compositional information only! The value was based on duplicate analyses performed in a "quick and dirty" manner.

(2) The main advantage that compositional reference materials offer over primary reference standards is that they provide a better match to sample composition. They are a tool for minimizing "matrix" or inter-element effects or identifying shortcomings in the analytical method such as incomplete decomposition, etc. The knowledgeable user thus strives to select compositional reference materials having certified elements at appropriate concentrations in a matrix as closely resembling the samples to be analyzed as possible.

Conversely, the user should be aware that the compositional reference materials may contain one or more elements which are not present in the samples but which could give rise to matrix or inter-element effects so that there is in effect no true matrix matching.

(3) In selecting a compositional reference material to match the matrix of his samples, the user should consider the magnitude of the certified value(s). There is a potential danger that, in preparing the solution of the reference material at the appropriate concentration for the element(s) of concern, the overall solution composition of the solution could differ significantly from that of the samples to be analyzed. This could apply equally to a high certified value which would require appreciable dilution of the prepared solution or a low certified value which would lead to a solution of higher concentration in matrix elements than found in the samples.

Other properties of compositional reference materials, equally important, to be considered by the user are, inter alia:

4. the period of validity of the certified values;
5. prescribed conditions for storage;
6. instructions for use such as:
    - minimum test portion amount,
    - use "as is" or "dry at 100°C, etc.;

7. certified values may be specific method dependent; and
8. magnitude of the uncertainty of the certified values.

(4) Many compositional reference materials are stable indefinitely. Examples are reference materials made from iron ore and siliceous material with no or low sulphide content. On the other hand, reference materials made from sulphide ores and concentrates may oxidize and therefore their certified values may have a limited period of validity. The user should not use a reference material for which the date of validity has passed.

(5) If a reference material has a defined period of validity, its useful lifetime may be unnecessarily shortened if the user does not adhere to the conditions prescribed for storage. A revised ISO Guide 31 "Contents of certificates of reference materials" will shortly be issued and it specifies that each reference material be assigned a period of validity. I wonder how many users have not succeeded in attaining a certified value within the stated uncertainty only ro discover that the date of validity has passed.

(6) In selecting a compositional reference material, the user should take into account the potential effect of test portion amount. If the test portion amount used to establish the homogeneity of the material was larger than the test portion amount intended by the user, the user could detect inhomogeneity. Similarly, the user could detect inhomogeneity even at the same test portion amount if his method has better precision that that used to establish homogeneity. In both instances, the detected homogeneity gives an uncertainty that must be added to the uncertainty of the certified value. The user should be aware that the uncertainty arising from the inhomogeneity could become sufficiently large that using only the statistical parameters of certification is no longer justified. The reference material is unsuitable for the intended purpose. This phenomenon can sometimes be observed in gold ores. An ore established to be homogeneous at one assay tonne can be experimentally shown to be inhomogeneous at smaller test portion amounts. As a result, when only one or two determinations are carried out at the smaller test portion, it may be observed that the value determined for gold amounts does not agree with the certified value within the stated uncertainty.

A similar problem may arise if the user's method requires a smaller test portion amount than is recommended by the producer of the compositional reference material for use in analysis.

(7) The user should be aware that when an element in a compositional reference material has been certified to a level of uncertainty by a specific method, it cannot be assumed that these quantities are necessarily applicable to his method, if different. The user should use this material to assess his performance for an element only where

the accuracy (trueness) and precision (repeatability) of his method are comparable to those of the method(s) used in certification.

(8) The magnitude of the uncertainty of the certified values of a compositional reference material can be an important consideration for the user. Indeed the user may have to consider the uncertainty in both the accuracy and the precision of his method in selecting suitable compositional reference materials. Because the issue is parallel for both accuracy and precision, I will discuss accuracy only.

Two cases are possible. The first occurs when the capability of the user's method is of better uncertainty in accuracy than the mean performance of the methods used in the certification of an element. Here the user in general passes the ISO Guide 33 statistical tests for the assessment of a method for accuracy. In fact however the user is evaluating his performance unrealistically and he should use a different reference material, one that has an uncertainty in the certified value that is commensurate with the capability of his method.

Related to this case is when the user must for some reason, e.g., a business agreement with a client or a need to demonstrate on-going validation of a method due to accreditation status, attain a defined level of accuracy in analysis, i.e. a defined level of uncertainty in accuracy. If the user chooses to prove this level through the use of compositional reference materials, he must select those materials with certified values with an uncertainty that permits this assessment. Of course, all this is meaningless if the user does not have a method capable of this level of accuracy.

The second occurs when the capability of the user's method is of worse accuracy than the mean performance of the methods used in the certification of an element. Here the user could fail the ISO Guide 33 statistical tests for the assessment of a method for accuracy. In fact however the user is evaluating his performance unrealistically and he should use a different reference material, one that has an uncertainty for the certified value that is commensurate with the capability of his method. A good example of the second case is the use of a compositional reference material certified for Ni by dimethylglyoxime precipitation, a very accurate and precise method, to assess the performance of a method that has an ICP-AES finish. The analyst would indeed be very hard pressed to obtain an uncertainty for accuracy and precision at the same level as the certified value.

I will revisit the implications of the two cases after the statistical tests for assessing the accuracy and precision of a method has been discussed below.

Assessment of Method for Accuracy and Precision of a Method

The use of compositional reference materials in mineral industry laboratories has increased appreciably during the past few years, mainly because of the increasing emphasis on and demand from the client for quality product or service, and also by the mounting acceptance by analytical laboratories of ISO quality systems for accreditation or certification. Fortunately the level of knowledge for using compositional reference materials to assess proficiency has increased corresponding but there still remain some misunderstandings on how to assess proficiency through statistical tests.

This part of the presentation presents how the user can assess the level of the performance of a method by applying the statistical tests in ISO Guide 33.

Precision (Repeatability) of a Method

To assess the precision (repeatability) of an analytical method by the analysis of a certified reference material, the average within-laboratory standard deviation of the certified value must be known and the user should have at least duplicate (2) results but preferably three or more.

The analytical method is accepted with regard to precision if:

$$(S_{wL}/\sigma_{Rm})^2 \leq (\chi^2_{n;\,0.95}/[n-1]) \qquad \text{Eq. 1}$$

where:

n	= the number of replicates (n should be ≥ 2),
S_{wL}	= the standard deviation of the replicate results,
σ_{Rm}	= the within-laboratory standard deviation of the certified value, and
$\chi^2_{n;\,0.95}$	= 0.95-quartile of the χ^2 distribution at n-1 degrees of freedom.

Note: In practice, this is not necessarily a very demanding test and a laboratory may want or be required to set tighter limits, for example, for Shewhart charts, business agreements, etc.

Accuracy of a Method

There still remains appreciable misunderstanding that the determined value of an element should lie within the 95% confidential intervals of the certified value for the element in a compositional reference material if the method is acceptable in terms of accuracy. While this is true, it is incorrect according to ISO Guide 33 "Uses of certified reference materials" and is also in conflict with the statistics. It should always be remembered that the 95% confidential intervals define the range if values that a certified value would be found 19 times if the interlaboratory certification programs were repeated 20 times under the same conditions. To be noted is that the magnitude of the 95% confidential intervals depends on the number of participating laboratories.

According to ISO Guide 33, the between-laboratories standard deviation of the certified value of a reference material must be known to assess the accuracy of a method. The method should be assessed on the basis of the mean value of two or more replicate results.

Two or More Replicate Analytical Results

If there are two (2) or more replicate results, the analytical method is accepted with regard to accuracy if:

$$|X_C - X_L| \leq 2\sqrt{\sigma_{Lm}^2 + S_{wL}^2/n} \qquad \text{Eq. 2}$$

X_C = the certified value,
σ_{Lm} = the between-laboratories standard deviation of the certified value,
X_L = mean value of the replicates, and
S_{wL} = standard deviation of X_L.

In many cases, $\sigma_{Lm} >> S_{wL}$, and/or $n > 3$ and Equation 2 can be approximated by:

$$|X_C - X_L| \leq 2\sigma_{Lm} \qquad \text{Eq. 3}$$

A spread of $\pm 2\ \sigma_{Lm}$ about the certified value contains 95% of the values used to estimate the certified value. About 5% of the accepted mean values lay outside this spread. Therefore, satisfying Equation 2 indicates that the value found by the method being tested would have been accepted in estimating in certified value of that element. In contrast, there is only a 5% probability that a result for a method that fails Equation 2 is in fact acceptable with respect to accuracy.

The 95% confidence intervals (C.I.) can be approximated by:

$$C.I. \approx \pm\ t_{0.975\ (k-1)} \cdot \sigma_{Lm} / \sqrt{k} \qquad \text{Eq. 4}$$

where:

k = the number of sets of results (laboratories) used to estimate the certified value; and

$t_{0.975\ (n-1)}$ = the 0.975 fractile of the Student distribution with (n-1) degrees of freedom. Its value can be approximated as "2" at $n \geq 10$.

If we compare Equations 2 or 3 with 4, we see that the C.I. is $\approx \sqrt{k}$ times smaller than the spread allowed by ISO Guide 33. This is why the user should not specifically aim to fall within the 95 % C.I. in assessing a method for accuracy. However if the users' method falls within the 95% C.I., so much the better! The following table which shows a comparison of the 95% C.I. and $2\ \sigma_{Lm}$ for some example elements in three compositional reference materials substantiates the $\sqrt{k}$ times relationship.

RM	Element	N	CV	95% C.I.	$2\ \sigma_{Lm}$
SU-1a	Ni	22	1.233%	0.008%	0.0322%
	Cu	24	0.967%	0.005%	0.0230%
	Co	20	0.041%	0.001%	0.004%
CH-3	As	10	143 µg/g	14 µg/g	39.6 µg/g
	S	18	2.82%	0.03%	0.094%
CZN-3	Zn	37	50.92%	0.08%	0.42%
	Ag	31	45 µg/g	2 µg/g	10 µg/g

A relationship that $\sigma_{Lm} \approx 2\,\sigma_{Rm}$ for the certified value is observed for many compositional reference materials although there is no theoretical or statistical basis for this. When the value of σ_{Lm} is unknown, the user may therefore assume that the method is accepted with regard to accuracy if:

$$|X_C - X_L| \leq 4\sigma_{Rm} \qquad \text{Eq. 4}$$

Note: The scope of the validity of this assumption is unknown and the user should be aware of the risk in accepting it. For example, the assumption is not valid for low level gold CCRMP reference materials such as GTS-2 and CH-3 for which $\sigma_{Lm} \approx \sigma_{Rm}$.

If neither σ_{Lm} nor σ_{Rm} are known, the laboratory could analyze the reference material at least in triplicate to provide a good estimate of S_{wL} which can be used as an approximation for σ_{Rm}. The method would therefore be accepted for accuracy if:

$$|X_C - X_L| \leq 4\,S_{wL} \qquad \text{Eq. 5}$$

Note: ISO/REMCO does not recommend the use of certified reference materials for which the uncertainty of certified values are not reported. This is usually found only for reference materials issued many years ago.

Single Analytical Result

If there is a single result, the analytical method is accepted with regard to accuracy if:

$$|X_C - X_L| \leq 2\sqrt{\sigma_{Lm}^2 + \sigma_{Rm}^2} \qquad \text{Eq. 6}$$

As above, if $\sigma_{Lm} >> S_{wL}$, the analytical method is accepted with regard to accuracy if the condition in Equation 3 is met:

$$|X_C - X_L| \leq 2\sigma_{Lm} \qquad \text{Eq. 3}$$

If it is assumed that $\sigma_{Lm} \approx 2\,\sigma_{Rm}$, the analytical method is accepted with regard to accuracy if the condition in Equation 4 is met:

$$|X_C - X_L| \leq 4\,\sigma_{Rm} \qquad \text{Eq. 4}$$

Similarly when σ_{Lm} of the certified reference material is not known, the analytical method is accepted with regard to accuracy based on a single result according to Equation 4. The following are two examples of assessing a method for accuracy and precision using two CCRMP gold ore compositional reference materials, MA-1b and CH-3.

Gold Ore, MA-1b

Au Value				
Certified Value	**95% C.I.**	σ_{Lm}	σ_{Rm}	
17.0 µg/g	0.3 µg/g	0.70 µg/g	0.42 µg/g	$\sigma_{Lm} \approx 2\,\sigma_{Rm}$

	Laboratory A	**Laboratory B**	
Mean Value, X_L	18.6 µg/g (1)*	17.12 µg/g (5)*	( )* = replicates
St'd Dev., S_{wL}		0.49 µg/g	

		Laboratory A	**Laboratory B**	
	$\lvert X_C - X_L \rvert$	1.6 µg/g	0.12 µg/g	
Eq. 1	$(S_{wL}/\sigma_{Rm})^2$		1.38	1.38 < 2.78
Eq. 1	$(\chi^2_{n\ 0.95}/[n-1])$		2.78	
Eq. 2	$2\sqrt{\sigma_{Lm}^2 + S_{wL}^2/n}$		1.47 µg/g	
Eq. 5	$4\,S_{wL}$		1.96 µg/g	
Eq. 6	$2\sqrt{\sigma_{Lm}^2 + \sigma_{Rm}^2}$	1.63 µg/g		
Eq. 4	$4\,\sigma_{Rm}$	1.68 µg/g		

- Laboratory A and B are accepted with respect to accuracy.
- Laboratory B is accepted with respect to precision.

Note: Laboratory B also falls within the 95% C.I whereas Laboratory A does not but is still accepted with regard to accuracy

Gold Ore, CH-3

Au Value				
Certified Value	**95% C.I.**	σ_{Lm}	σ_{Rm}	
1.40 µg/g	0.30 µg/g	0.07 µg/g	0.11 µg/g	$\sigma_{Lm} \approx \sigma_{Rm}$

	Laboratory A	Laboratory B
Mean Value, X_L	1.15 µg/g (1)*	1.78 µg/g (3)*
St'd Dev., S_{wL}		0.082 µg/g

		Laboratory A	Laboratory B	
	$\lvert X_C - X_L \rvert$	0.25 µg/g	0.38 µg/g	
Eq. 1	$(S_{wL}/\sigma_{Rm})^2$		0.56	0.56 < 3.91
Eq. 1	$(\chi^2_{n;\,0.95}/[n-1])$		3.91	
Eq. 2	$2\sqrt{\sigma_{Lm}^2 + S_{wL}^2/n}$		0.17 µg/g	
Eq. 5	$4\,S_{wL}$		0.33 µg/g	
Eq. 6	$2\sqrt{\sigma_{Lm}^2 + \sigma_{Rm}^2}$	0.26 µg/g		
Eq. 4	$4\,\sigma_{Rm}$	0.44 µg/g		

- Laboratory A is accepted with respect to accuracy.
- Laboratory B is unsatisfactory with respect to accuracy.
- Laboratory B is accepted with respect to precision.

Note: Neither laboratory falls within the 95% C.I but Laboratory A is still accepted with regard to accuracy

Let's return to discuss the implication of the relative magnitudes of the uncertainty in accuracy of the reference material and the method being assessed. Figures 1a and 1b pertain to when the uncertainty in accuracy of the reference material is better than that of the method. Figure 1a depicts where the method is acceptable with regard to accuracy, i.e., the value determined by the method falls within $\pm 2\sigma_{Lm}$ of the certified value. Figure 1b depicts where the value determined by the method is rejected with regard to accuracy, i.e., the value determined by the method does not fall within $\pm 2\sigma_{Lm}$ of the certified value. In fact however, the greater uncertainty of the method renders this test invalid. A good analogy is trying to measure an item several meters in length with a gauge of lesser length and that is marked only in centimeters. The wrong tool has been used! The user should have selected a reference material for which the uncertainty in the certified value such that $2\sigma_{Lm} \approx 4S_w$.

Figures 2 pertains to when the uncertainty in accuracy of the method is better than that of the reference material. In this instance however Figures 2a and 2b both depict that the method is acceptable with regard to accuracy, i.e., the value determined by the method falls within $\pm 2\sigma_{Lm}$ of the certified value. The greater uncertainty of the reference material renders this test invalid. A good analogy is trying to measure an item that is only several centimeters in length with a gauge of greater length and that is marked only in meters. As above, the wrong tool has been used! The user should have selected a reference material for which the uncertainty in the certified value such that $2\sigma_{Lm} \approx 4S_w$.

Gold ore MA-1b can be used to illustrate the above. A quick calculation shows that $2\sigma_{Lm}$ is ~8.1% of the certified value, i.e., MA-1b allows the user to assess accuracy to no better than 8.2%. If the user must demonstrate that his method gives an accuracy better than ~8.1%, e.g., ± 5%, he should select a different certified gold ore for which $2\sigma_{Lm} \leq 5\%$. On the other hand, if the user's method gives no better than ± 8%, MA-1b is a suitable reference material.

Long Term Assessment of a Method

The statistical tests in ISO Guide 33 provide a snap shot of method performance, i.e., a one time event. What can be done if a laboratory analyzes a given compositional reference materials by the same method several times over the course of time? The method can be assessed at each analysis episode with the tests in ISO Guide 33 but there might be other important information to be learned on method performance if all the analyses together were tied together. This is a discussion for another time.

References

ISO Guide 33	Uses of Certified Reference Materials
ISO Guide 34	General requirements for the competence of reference materials Producers

CANMET Report SU-1a
CANMET Report CH-3
CANMET Report CZN-3

List of Figures

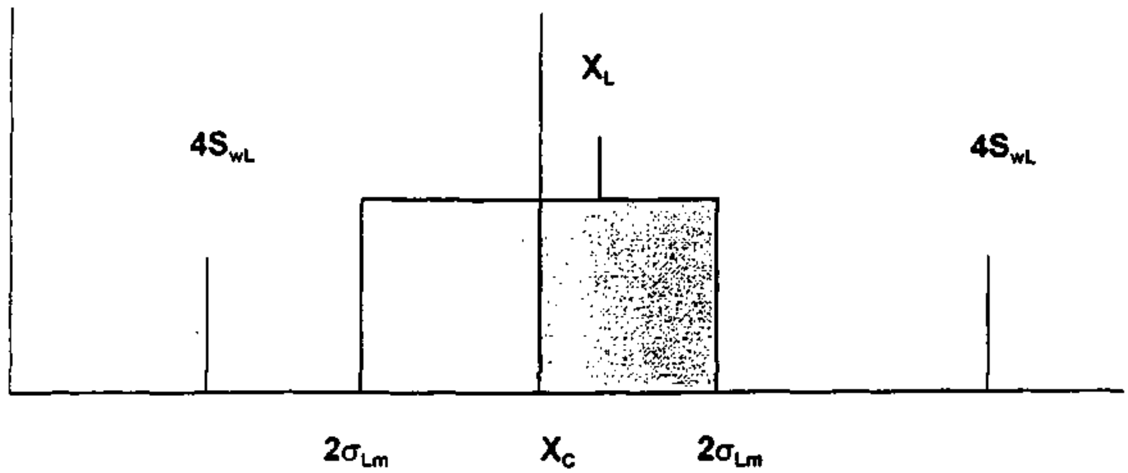

Figure 1a: Case 1: Uncertainty of C.V. < users' method

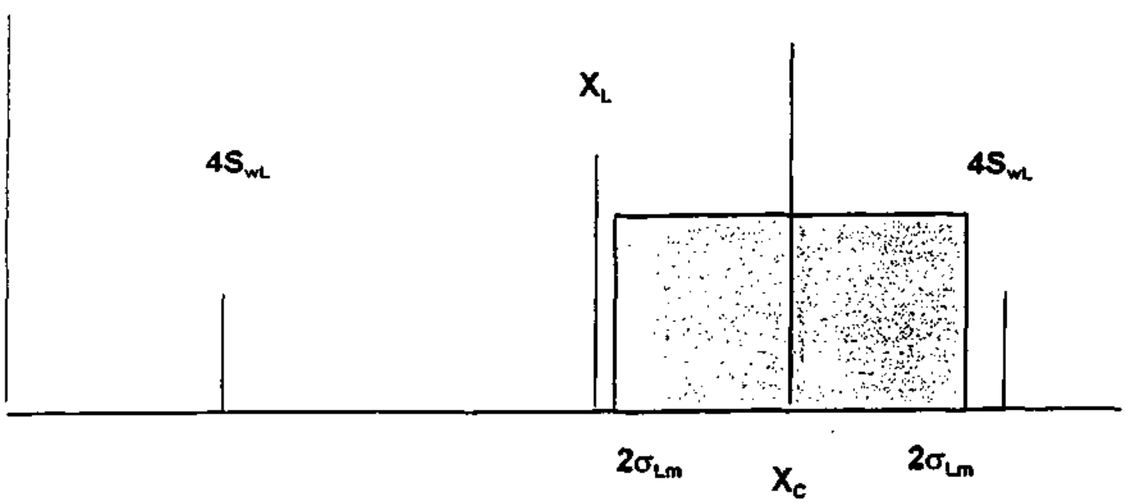

Figure 1b: Case 1: Uncertainty of C.V. < users' method

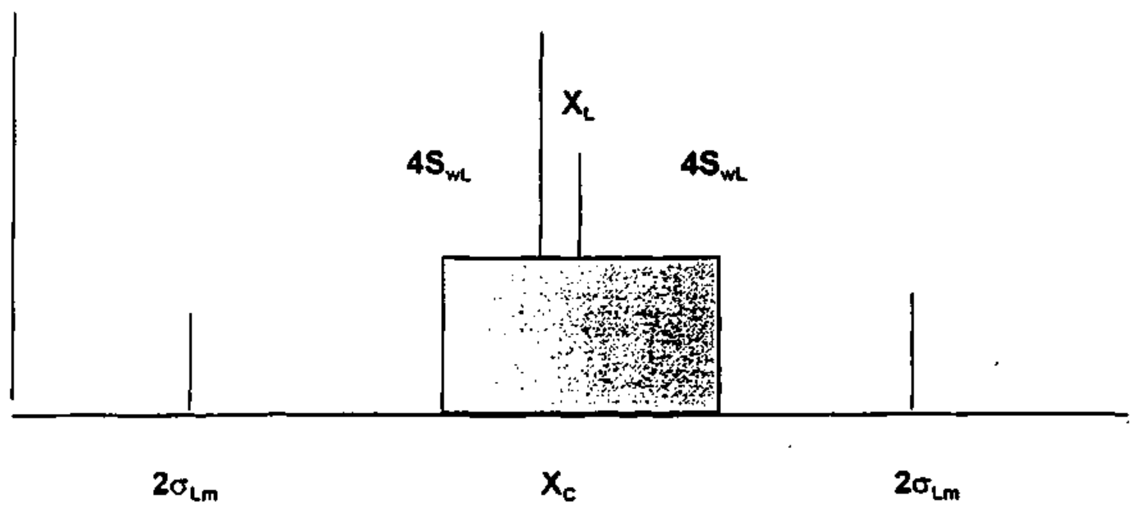

Figure 2a: Case 2: Uncertainty of C.V. > users' method

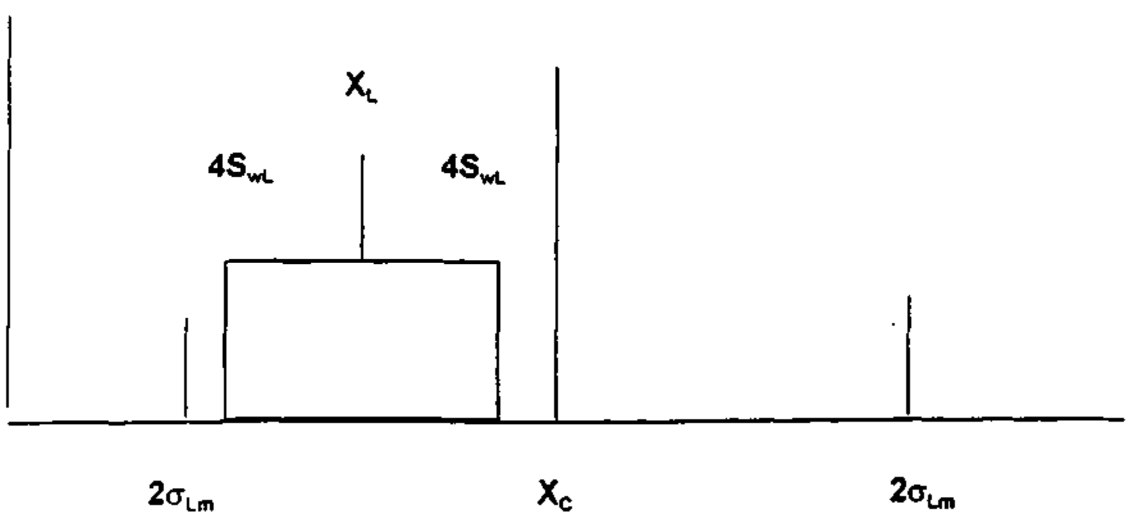

Figure 2b: Case 2: Uncertainty of C.V. > users' method